GOVERNMENT OF INDIA, THE PATENT OFFICE
214, ACHARYA JAGADISH BOSE ROAD
CALCUTTA-700017.

Complete Specification No. 154647 dated 12th August, 1981.

Application and Provisional Specification No. 907/Cal/81 dated 12th Aug., 1981.

Acceptance of the complete specification advertised on 24th November, 1984.

Index at acceptance— 32F3b [IX(1)]

International Classification— C11c 3/10.

Process for preparing derivatives of castor oil

The Alkali and Chemical Corporation of India Limited, an Indian Company, of ICI House, 34 Chowringhee Road, Calcutta-700071, West Bengal, India.

The following specification describes the nature of this invention.

 PRICE: TWO RUPEES

This invention has been conceived by Dr. Annoottam Ghosh.

The present invention relates to a process for preparing novel derivatives of castor oil, and their subsequent polymerisation in emulsion, solution and bulk.

The polymers which are also novel, have potential applications in the adhesives and surface coatings industries. In particular, the solution copolymers have outlets as adhesives or lacquers. The emulsion coplymers are useful as vehicles for emulsion paints.

These polymerisable derivatives of castor oil may be synthesised by reacting castor oil with an acrylic acid of the following formula:

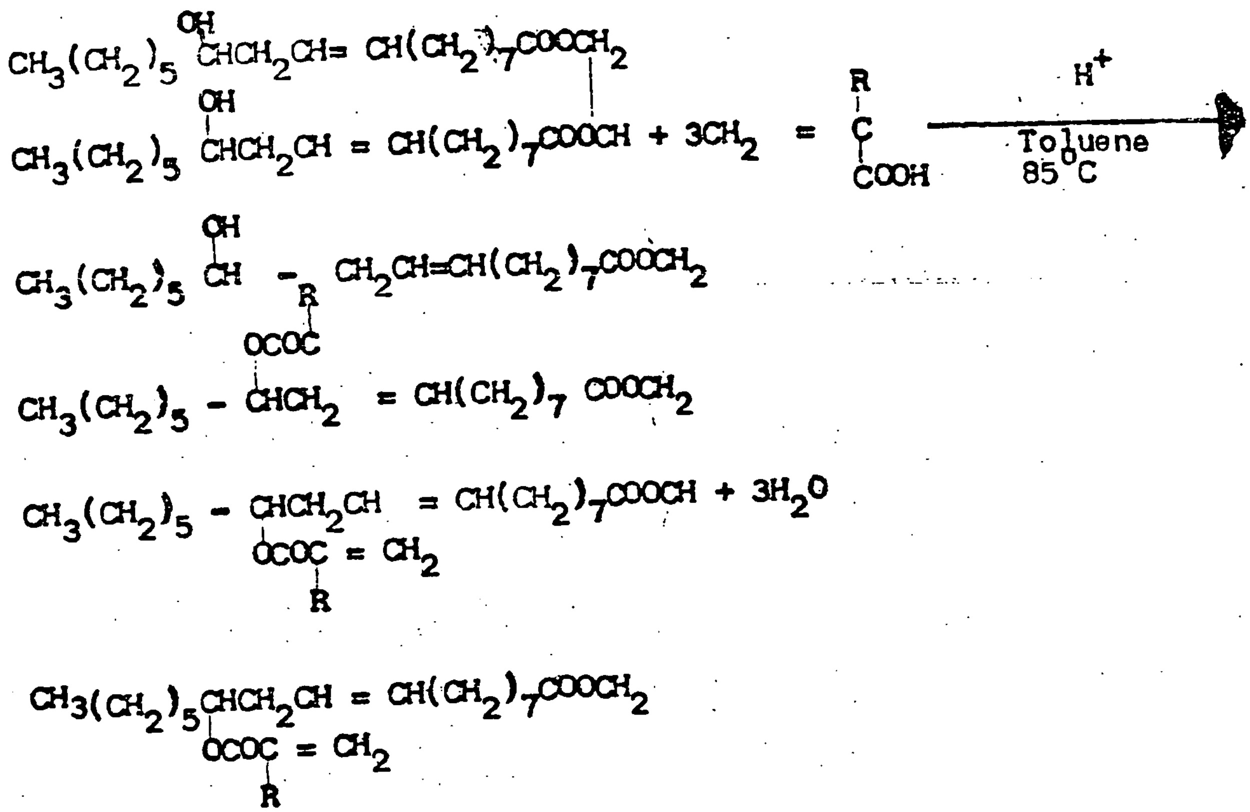
$$CH_2 = \underset{\displaystyle R}{\underset{|}{C}} - COOH$$

where R is H or CH_3,

in the presence of a trade a trace of nineral acid as catalyst. The water liberated furing the reaction is removed continuously by azeotropic distillation with toluene at about 85°C as outlined below in the reaction scheme.

The process for preparation of these novel derivatives is illustrated by the following reaction scheme. In this scheme, castor oil is represented by the triglyceride of ricinoleic acid, whhich constitutes about 85% of triglycerides present in castor oil. The remaining triglycerides take no part in the esterification reaction.

Reaction Scheme :



ACRYLATED OR METHACRYLATED CASTOR OIL

R is H or CH_3

The number of moles of the acrylic acid or methacrylic acid can be varied between 0 moles to 3 moles, accordingly the degree of substitution varies between 0 and 2.8.

EXAMPLE 1

1864 parts by weight of castor oil was mixed with 432 parts by weight of acrylic acid and to this was added 92 parts by weight of tolume. A trace of concentrated sulfuric acid (0.01% with respect to the castor oil) was

added to catalyse the reaction. 0.1% hydroquinone was added as an inhibitor, so that the homopolymerisation of acrylic acid is suppressed and the whole reaction mixture was heated in a three-necked round bottom flask equipped with a mechanical stirrer and the Dean-Stark assembly. The water formed during the reaction formed an azeotrope with tolune which came over at 85°C. The total amount of water collected was 108 ml. which was equal to the stoichimometric amount. The reaction was carried out for 4½ hours.

The yield was found to be about 95% and the product was characterised by infra-red spectroscopy. The hydroxyl values indicated the functionality of the product to be approximately 2.8.

EXAMPLE 2

1864 parts by weight of castor oil was mixed with 206.4 parts by weight of methacrylic acid, in a three-necked round bottom flask equipped with a mechanical stirrer and the Dean-Stark assembly. A trace of concentrated sulfuric acid (0.01%) was added as a catalyst.).1% of hydroquinone was added as an inhibitor so that the homopolymerisation of methacrylic acid is supporessed, and 30.3 parts by weight of tolunene was added to form an azeotrope with the water formed during the course of the reaction. The azeotrope started coming over at 85°C. The total amount of water collected was 36 ml. The reaction was carried out for 5 hours. The yield was found to be about 95% and the product was characterised

by infra-red spectroscopy. The functionity of the product was found to be approximately 1.

POLYMERISATION STUDIES

Emulsion hompolymerisation or copolymerisation of the above monomers with common cinyl monomers such as methyl methacrylate, styrene or cinyl acetate was carried out with a free radical initiator at 85°C for 4 hours.

SOlution polymerisation of the above monomers was carried out in the usual prganic solvents such as ethyl acetate, ethanol, acetone at 70-80°C with a free radical initiators.

EXAMPLE 3

SOLUTION COPLYMERISATION

6 parts by weight of acrylated castor oil and 14 parts by weight of methyl methacrylate and 0.8 parts by weight of 2,2' azobis-iso butyronitrile and 80 parts by weight ethyl acetate were heated together for 4½ hours at 78°C in N_2 atmosphere to give a solution copolymer of average molecular weight of 14,000 and conversion of monomer to polymer was found to be 91.2% Glass transition measurements were carried out on the polymers. Only one transition was observed indicating that a genuine copolymer had been formed and not a mixture of two homopolymers. The soltion copolymer

may be used as such or the solvent may be evaporated off yielding the solid copolymer.

Similar reaction in case of methacrylated castor oil gave a copolymer of average molecular weight of 8,00, the conversion of monomer to polymer being 93.4% and only one glass transition was observed.

EXAMPLE 4

8 parts by weight of methacrylated castor oil (degree of substitution 1) and 12 parts by weight of methyl methacrylate and 0.8 parts by weight of 2,2' azobis-iso-butyronitrile and 80 parts by weight of ethyl acetate were heated together for 4½ hours at 75°C in a N_2 atmosphere to give a solution copolymer of average molecular weight of 15,800 and conversion of monomer to polymer was found to be 86.7%.

Glass transition studies were carried out on these polymers. Since only one transition was observed, it is indicated that a genuine copolymer had been formed and not a mixture of two homopolymers.

Similar reaction in case of acrylated castor oil gave a copolymer of average molecular weight 13,000, the conversion being 90.7% and only one glass transition was observed.

The solution copolymers may be used as such or the solvent can be evaporated off to give a solid copolymer.

EXAMPLE 5

10 parts by weight of acrylated castor oil (degree of substitution 2) 10 parts by weight of methyl methacrylate and 0.8 parts by weight of 2,2' azobis-isobutyronitrile and 80 parts by weight of ethyl acetate were heated together at about 75°C, for 4½ hours in a N_2 atmosphere. The resulting solution copolymer had an average molecular weight of 18, 700, the conversion being 91%.

Glass transition studies were carried out with these polymers and since only one transition was observed it is indicated that a genuine copolymer had been formed and not a mixture of two homopolymers. Similar reactions with methacrylated castor oil gave a copolymer of average molecular weight of 15,000, the conversion being 91.8% and only one glass transition was observed.

The solution copolymers may be used as such or the solvent can be evaporated off to give a solid copolymer.

EXAMPLE 6

EMULSION COPOLYMERISATION

Emulsion copolymerisation of acrylated castor oil (degree of substitution 2) and methyl methacrylate was carried out as described below.

30 parts by weight of methyl methacrylate and 23 parts by weight of castor oil, were emulified with 46 parts by weight of tap water containing 2 parts by weight nonionic

surfactant and 0.2 parts by weight anionic surfactant and 0.3 parts by weight sodium carboxy methyl methyl cellulose and 0.6 parts by weight potassium persulphate. The emulsiofication was carried out by stirring at 200 r.p.m. The stirred reaction mixture was heated at 85°C for 5 hours under nitrogen, and the emulsion copolymer product was formed. The averagemolecular weight of the copolymer was found to be 115,000, and a vonversion of monomer to polymer of 94%.

G lass transition stufied showed only one transition, indicating that a genuine copolymer had been formed and not a mixture of two hompolymers.

The emulsion copolymer may be used as such or the water may be evaporated off leaving the solid copolymer.

Similar experiments were carried out with methacrylated castor oil and the product gave an average molecular weight of 150000.

Glass transition studies were carried out and since only one transition was observed, it is indicated that a genuine copolymef had been formed and not a mixture of two homopolymers.

The emulsion copolymer may be used as such or the water may be evaporated off to yield a solid polymer.

EXAMPLE 7

BULK CO POLYMERISATION

50 parts by weight of acrylated castor oil (degree of substitution 2.8) 50 parts by weight of methyl methacrylate and 0.4 parts by weight of 2,2' azobis-isobutyronitrile were heated to 75°C with magnetic stirring. The reaction was carried out for 4½ hours giving a solid copolymer having an average molecular weight of 58,000, conversion of monomer to polymer was 74.3%.

Glass transition studies were carriedout and since only one transition was observed it indicated that a genuine copolymer had been formed and not a mixture of two homopolymers.

Similar experiment with methacrylated castor oil gave a solid of an average molecular weight of 45,000 and conversion of monomer to polymer was 66.5%.

Dated this 10th day of August, 1981.

Sd/-
A.V.Nathan
of Remfry & Son
Agent for the Applicants.

154647

THE PATENTS ACT, 1970

COMPLETE SPECIFICATION

(Section—10)

Process for preparing derivatives of castor oil.

The Alkali and Chemical Corporation of India Limited, an Indian Company, of ICI House, 34 Chowringhee Road, Calcutta-700071, West Bengal, India.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

This invention has been conceived by Dr. Annbottam Ghosh.

The present inventon relates to a process for preparing novel derivatives of castor oil, and their subsequent polymerisation in emulsion, solution and bulk.

The polymers which are also novel, have potential applications in the adhesives and surface coatings industries. In particular, the solution copolymers have outlets as adhesives or lacquers. The emulsion copolymers are useful as vehicles for emulsion paints.

These polymerisable derivatives of castor oil may be synthesised by reacting castor oil with an acrylic acid of the following formula:

$$CH_2 = \underset{\displaystyle R}{\underset{|}{C}} - COOH$$

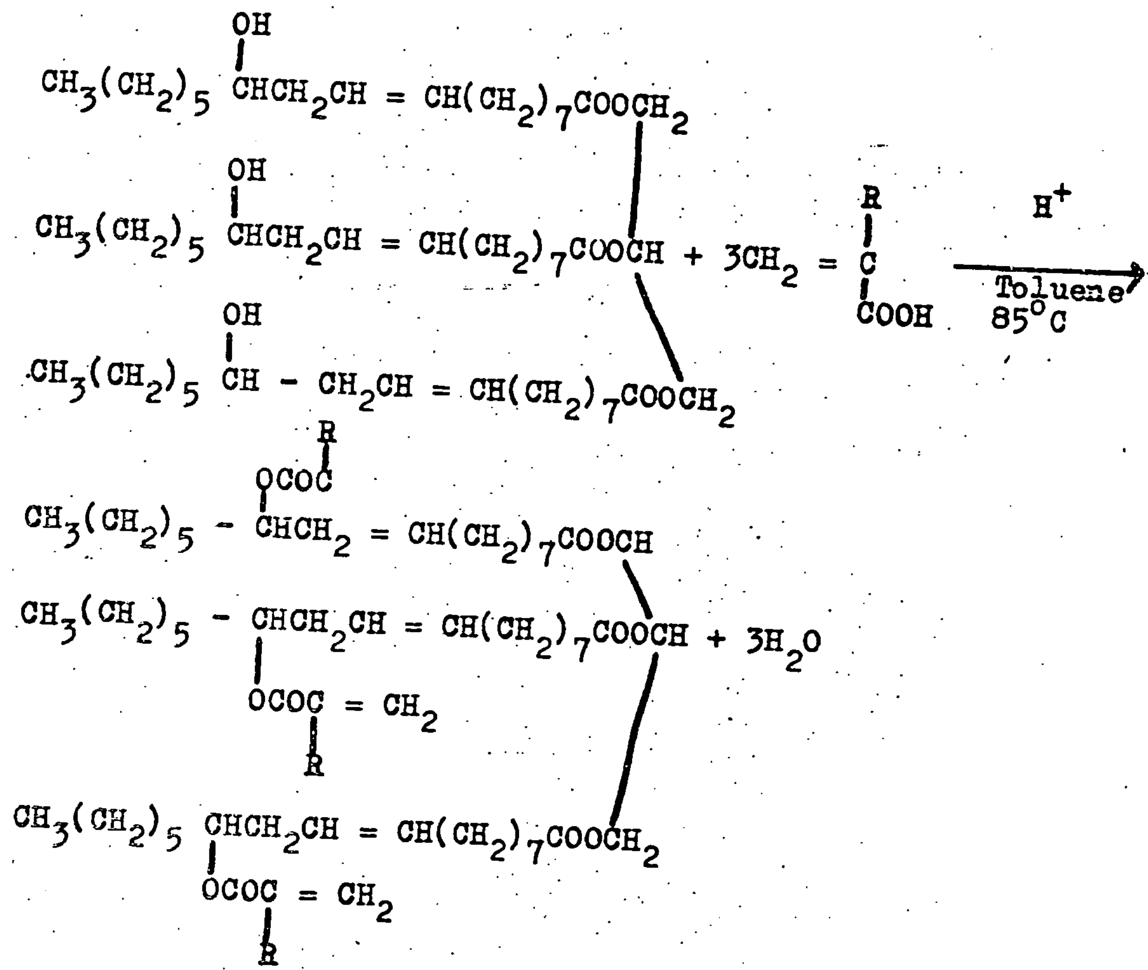
where R is H or CH_3,

in the presence of a trace of mineral acid as catalyst. The water liberated furing the reaction is removed continuously by azeotropic distillation with toluene at about 85°C as outlined below in the reattion scheme.

71

The process for preparation of these novel derivatives is illustrated by the following reaction scheme. In this scheme, castor oil is represented by the triglyceride of ricinoleic acid, which constitutes about 85% of triglycerides present in castor oil. The remaining triglycerides take no part in the esterification reaction.

Reaction Scheme:



ACRYLATED OR METHACRYLATED CASTOR OIL

R is H or CH_3.

The number of moles of the acrylic acid or methacrylic acid can be varied between 0 moles to 3 moles, accordingly the degree of substitution varies between 0 and 2.8.

Accordingly, the present invention provides a process for preparing novel derivatives of castor oil which comprises reacting castor oil with acrylic acid of the following formula:

$$CH_2 = \underset{\displaystyle R}{\underset{|}{C}} - COOH$$

wherein R is H or CH_3 in the presence of a trace mineral acid and removing the water liberated in the reaction by known means.

The mineral acid used in the reaction may be concentrated sulphuric acid.

The following examples illustrate the invention and should not be considered limitative.

EXAMPLE 1

1864 parts by weight of castor oil was mixed with 432 parts by weight of acrylic acid and to this was added 92 parts by weight of toluene. A trace of concentrated sulphuric acid (0.01% with respect to the castor oil) was added to catalyse the reaction. 0.1% hydroquinone was added as an inhibitor, so that the homopolymerisation of acrylic acid is suppressed and the whole reaction mixture was heated in a three-necked round bottom flask equipped with a mechanical stirrer and the Dean-Stark assembly. The water formed during the reaction formed an azeotrope with toluene which came over at 85°C. The total amount of water collected was 108 ml., which was equal to the stoichiometric amount. The reaction was carried out for 4 1/2 hours.

The yield was found to be about 95% and the product was characterised by infra-red spectroscopy. The hydroxyl

values indicated the functionality of the product to be approximately 2.8.

EXAMPLE 2

1864 parts by weight of castor oil was mixed with 206.4 parts by weight of methacrylic acid, in a three-necked round bottom flask equipped with a mechanical stirrer and the Dean-Stark assembly. A trace of concentrated sulfuric acid (0.01%) was added as a c atalyst. 0.1% of hydropquinone was added as an inhibitor so that the homppolymerisation of methacrylic acid is suppressed, and 30.3 parts by weight of toluene was added to form an azeotrope with the water formed during the course of the reaction. The azeotrope started coming over at 85°C. The total amount of water collected was 36 ml. The reaction was carried out for 5 hours. The yield was found to be about 95% and the product was characterised by infra-red spectroscopy. The functionality of the product was found to be approximately 1.

POLYMERISATION STUDIES

Emulsion homopolymerisation or copolymerisation of the above monomers with common vinyl monomers such as methyl methacrylate, styrene or cinyl acetate was carried out with a free radical initiator at 85°C for 4 hours.

Solution polymerisation of the above monomers was carried out in the usual organic solvents such as ethyl acetate, ethanol, acetone at 70-80°C with a free radical initiator.

EXAMPLE 3

SOLUTION COPOLYMERISATION

6 parts by weight of acrylated castor oil and 14 parts by weight of methyl methacrylate and 0.8 parts by weight of 2,2' azobis-iso butyronitrile and 80 parts by weight of ethyl acetate were heated together for 4½ hours at 78°C in N_2 atmosphere to give a solution copolymer of average molecular weight of 14,000 and conversion of monomer to polymer was found to be 91.2% Glass transition measurements were carried out on the polymers. Only one transition was observed indicating that a genuine copolymer had been formed and not a mixture of two homppolymers. The solution copolymer may be used as such or the solvent may be evaporated off yielding the s olid copolymer.

Similar reaction in case of methacrylated castor oil gave a copolymer of average molecular weight of 8,000 the conversion of monomer to polymer being 93.4% and only one glass transition was observed.

EXAMPLE 4

8 parts by weight of methacrylated castor oil (degree of substitution 1) and 12 parts by weight of methyl methacrylate and 0.8 parts by weight of 2,2' azobis-iso-butyronitrile and 80 parts by weight of ethyl acetate were heated together f or 4½ hours at 75°C in a N_2 atmosphere to give a solution copolymer of average molecular weight of 15,800 and conversion of monomer to polymer was found to be 86.7%.

Glass transition studies were carried out on these polymers. Since only one transition was observed, it is indicated that a genuine copolymer had been formed and not a mixture of two homppolymers.

Similar reaction in case of acrylated castor oil gave a copolymer of average molecular weight 13,000, the conversion being 90.7% and only one glass transition was observed.

The solution copolymers may be used as such or the solvent can be evaporated off to give a solid copolymer.

EXAMPLE 5

10 parts by weight of acrylated castor oil (degree of substitution 2) 10 parts by weight of methyl methacrylate and 0.8 parts by weight of 2,2' azobis-isobutyronitrile and 80 parts by weight of ethyl acetate were heated together at about 75°C, for 4½ hours in a N_2 atmosphere. The resulting solution copolymer had an average molecular weight of 18,700, the conversion being 91%.

Glass transition studies were carried out with these polymers and since only one transition was observed it is indicated that a genuine copolymer had been fomred and hot a mixture of two homppolymers. Similar reactions with methacrylated castor oil gave a copolymer of average molecular weight of 15,000, the conversion being 91.8% and only one glass trasnsition was observed.

The solution copolymers may be used as such or the solvent can be evaporated off to give a solid copolymer.

EXAMPLE 6

EMULSION COPOLYMERISATION

Emulsion copolymerisation of acrylated castor oil (degree of substitution 2) and methyl methacrylate was carried out as described below.

30 parts by weight of methyl methacrylate and 23 parts by weight of acrylated castor oil, were emulsified with 46 parts by weight of tap water containing 2 parts by weight of nonionic surfactant a nd 0.2 parts by weight of anionic surfactant and 0.3 parts by weight of sodium carboxy methyl cellulose and 0.6 parts by weight of potassium persulphate. The emulsification was carried out by stirring at 200 r.p.m. The stirred reaction mixture was heated at 85°C for 5 hours under nitrogen, and the emulsion copolymer product was fomred. The average molecular weight of the copolymer was found to be 115,000, and a conversion of monomer to polymer of 94%.

G lass transition studies showed only one transition, indicating that a genuine copolymer had been formed and not a mixture of two hompolymers.

The emulsion copolymer may be used as such or the water may be evaporated off leaving the solid copolymer.

Similar experiments were carried out with methacrylated castor oil and the product gave an average molecular weight of 150,000.

G lass transition studies were carriedout and sine only one transition was observed, it is indicated that a genuine copolymer had been formed and not a mixture of two homopolymers.

The emulsion copolymer may be used as such or the water may be evaporated off to yield a solid polymer.

EXAMPLE 7

BULK COPOLYMERISATION

50 parts by weight of acrylated castor oil (degree of substitution 2.8) 50 parts by weight of methyl methacrylate and 0.4 parts by weight of 2,2' azobis-isobutyronitrile were heated to 75°C with magnetic stirring. The reaction was carried out for 4½ hours giving a solid copolymer having an average molecular weight of 58,000, conversion of monomer to polymer was 74.3%.

Glass transition studies were carried out and since only one tr nsition was observed it is indicated that a genuine copolymer had been formed and not a mixture of two homopolymers.

Similar experiment with methacrylated castor oil gave a solid of an average molecular weight of 45,000 and conversion of monomer to polymer was 66.5%.

We Claim:- **154647**

1. A process for preparing novel derivatives of castor oil which comprises reacting castor oil with acrylic acid of the following formula:

$$CH_2 = \underset{\displaystyle R}{\underset{|}{C}} - COOH$$

wherein R is H or CH_3 in the presence of a trace mineral acid and removing the water liberated in the reaction by known means.

2. A process according to claim 1, wherein said mineral acid is concentrated sulphuric acid.

3. A process for preparing novel derivatives of castor oil substantially as herein described and with reference to the foregoing examples.

Dated this 2nd day of August, 1982.

(A. GABRIEL)
of REMFRY & SON
AGENT FOR THE APPLICANTS